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Gas sensing properties of individual composite nanostructures TiO_{2-x}/MWCNT and SnO_x/MWCNT measured by scanning force microscopy

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Composite nanomaterials based on multi-walled carbon nanotubes (MWCNT) and metal oxides are promising materials for gas-sensing application [1]. The trend of miniaturization of electronic devices and the fundamental replacement of massive layers by nanoscale elements attract great interest in the study of electron transport processes in individual nanostructures. Scanning force microscopy is effective method to study the electrical properties of individual nanostructures [2, 3].

MWCNTs synthesized by chemical vapor deposition were used in the work. The concentration of nitrogen in nanotube walls is 3.7 at.% according to X-ray photoelectron spectroscopy data. The functionalization of as-grown MWCNTs was carried out by irradiation with argon ions with energy 5 keV and ion dose 10^{16} cm^{-2}. Composite nanostructures of metal oxide/MWCNTs were fabricated by deposition of non-stoichiometric titanium dioxide (TiO_{2-x}) and tin oxide (SnO_x) on the surface of functionalized MWCNTs using magnetron sputtering method.

Individual MWCNTs, TiO_{2-x}/MWCNTs, and SnO_x/MWCNTs were deposited on microelectrode array from suspensions by spin coating. The suspensions of nanotube and nanostructures was obtained by ultrasonic dispersion of the layers in dichloromethane for 20 min. Conductive atomic force microscopy (C-AFM) and electrostatic force microscopy (EFM) measurements were performed using an atomic force microscope MFP-3D SA (Asylum Research) with conductive cantilevers HA_FM/Pt (NT-MDT) in dry nitrogen (RH ~ 2%) at room temperature. Gas sensing properties were investigated on exposure to a reducing gas (ammonia) and an oxidizing gas (nitrogen dioxide) with concentrations of 1000 ppm.

Optical and atomic-force microscopes were used to detection of individual MWCNTs and composite nanostructures located on two adjacent electrodes (Fig. 1).

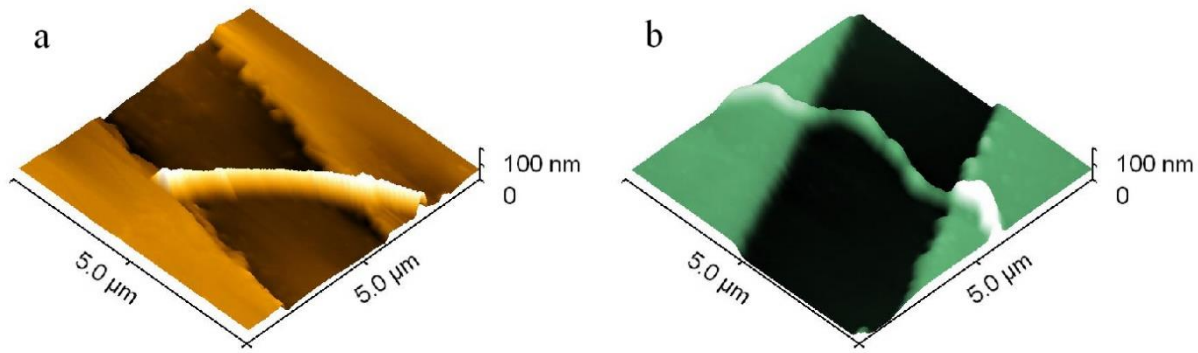

Figure 1. AFM images of individual composite nanostructures located on two adjacent microelectrodes for (a) TiO_{2-x}/MWCNT and (b) SnO_x/MWCNT.

Using the values of work function for the samples obtained by technique [4], the mean values of the Fermi level shift upon adsorption of ammonia and nitrogen dioxide was determined (Fig. 2a).

By comparing the work function values for highly oriented pyrolytic graphite as calibration sample and MWCNTs, it was found that argon ions forms acceptor-like defects in nanotube walls and holes become the major charge carriers in functionalized MWCNTs. During adsorption of the reducing gas, the Fermi level shift in MWCNTs increases slightly due to partial recombination of

holes with electrons. In the case of adsorption of the oxidizing gas, the Fermi level shift decreases significantly, which is caused by an increase the holes concentration in the MWCNT walls.

The Fermi level shift in TiO_{2-x}/MWCNTs is like functionalized MWCNTs, but in contrast to MWCNTs, the titanium oxide is an n-type semiconductor and major charge carriers therein are electrons.

In the SnO_x/MWCNTs nanostructure the Fermi level shift during gas adsorption is the opposite. Tin oxide is a wide band-gap semiconductor, a space charge region is formed on the band diagram due to surface states, which leads to a pinning of the Fermi level in the depth of band gap. As a result of adsorption of the oxidizing gas, electrons from deep acceptor levels transfer to adsorbate energy levels. The positive charge of surface defect states which occurs after leaving of electrons can partially compensate for the surface negative charge and lead to an increase in the Fermi level shift upwards.

The mean value and range of the conductance of individual MWCNTs, TiO_{2-x}/MWCNTs and SnO_x/MWCNTs nanostructures upon exposure to gases based on C-AFM measurements was determined (Fig. 2b). The electrical conductance of individual TiO_{2-x}/MWCNTs and SnO_x/MWCNTs equal in the order of magnitude to the conductance of individual nanotubes that indicates on contribution of the MWCNT walls to the total conductance of composite nanostructures. The changes in conductance during gas exposure correspond to the change in the Fermi level shift for individual MWCNTs, TiO_{2-x}/MWCNTs and SnO_x/MWCNTs nanostructures.

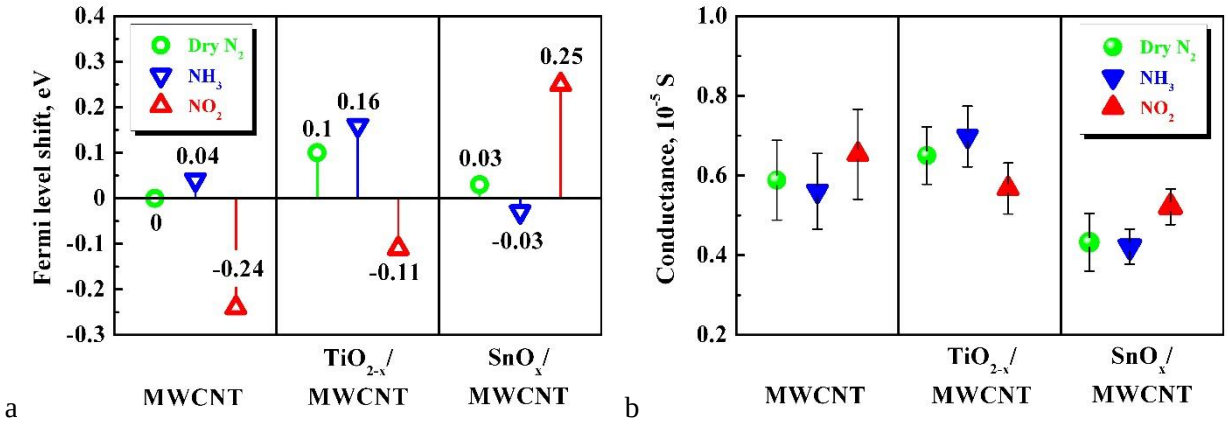

Figure 2. Characteristics of individual MWCNTs, TiO_{2-x}/MWCNTs and SnO_x/MWCNTs in dry nitrogen, ammonia and nitrogen dioxide: (a) mean on the value of Fermi level shift relative to its position in MWCNT; (b) mean and range on the value of conductance.

The work was carried out according to the state task of the Omsk Scientific Center SB RAS (project registration number AAAA-A17-117041210227-8).

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